WATERAGRI

D4.4 Description of Developed Membrane-based Solution for Nutrient Recovery

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WP 4 Nutrient Recovery from Streams

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Abstract:	Nutrient recovery from agricultural runoff with biobased membranes offers an innovative approach enabling the return of the leached nutrients back to the cultivation and their original purpose, which is fertilising. However, the concept is very new and needs further fine-

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Contents

List of tables

List of figures

List of Abbreviations and Acronyms	
CNF	Cellulose Nanofibrils
DS	Degree of substitution
GTAC	Glycidyl trimethylammonium chloride
SutCo	Surface treatment Concept
XPS	X-ray photoelectron spectroscopy
AGU	Anhydroglucose unit

1. Introduction

Numerous locations globally are facing problems with impaired water quality and eutrophication caused by the abundant use of fertilisers. The higher amount of nutrients applied to crops implies a high risk of environmental pollution from runoff (Zuazo et al. 2004, Divya & Belagali 2012). The migration of nutrients through sediments and runoff water not only declines soil fertility but also causes environmental problems when these nutrients are transported further downstream to lakes and reservoirs. Strategies and technologies to prevent these migrations are being developed, among others, wetlands (Fisher and Acreman 2004) and gypsum barriers (e.g., Ekholm 2020). Moreover, new innovative solutions are evolving, aiming at overall sustainability in line with Europe's Circular Economy agenda emphasising recovery and reuse.

The abundance, renewability and environmentally benign character of cellulose as a raw material, as well as the numerous possibilities for its pre-treatment, disintegration and chemical modification, have contributed to the increasing interest in cellulose nano-fibrils (CNF) as a building block for the development of functional membranes for the removal of water-borne pollutants, e.g. heavy metal ions, natural organic matter, dyes, bacteria and viruses, selective oil recovery from oil–water mixtures, etc.

Cellulose nanofibrils (CNF) or nanocellulose (Figure 1) are rod-like nanoparticles with lengths varying between 100 and 2000 nm and diameters ranging between 2 and 20 nm, depending on the preparation route and origin of the cellulose. The combination of high strength, chemical inertness, hydrophilic surface chemistry, and high surface area makes nanocellulose a very promising material for high-performance membranes and filters in order to selectively remove contaminants from industrial and drinking waters. Nanocellulose with a high degree of crystallinity is chemically inert in aqueous media except at very high pH-values, and the intrinsic hydrophilicity of nanocellulose is shown to reduce bio-fouling and organic fouling. Defibrillation of cellulose fibre into nanocellulose results in a drastic increase in the available surface area. Depending on the preparation method, the specific surface area of nanocellulose can approach 500 m^2/g. This increase in surface area is related to an increase in the availability of the hydroxyl groups on the surface of nanocellulose, where functional groups or molecules can be grafted.

Figure 1. The appearance of cellulose nanofibrils (CNF) or nanocellulose (left) and the produced cationic nanocellulose-based nutrient-collecting membrane (right).

This report explains the development work carried out on using biobased membranes for nutrient recovery from agricultural runoff. Nanocellulose films were functionalised by the cationisation step for optimised affinity for primarily phosphate ions. Thereafter, a larger-scale membrane structure was prepared in VTT's semi-pilot line. Moreover, different configurations of the membrane sheet were exploited, aiming for a zero back-pressure system not interfering with natural flows and its performance in a real environment was tested in pilot wetland mesocosms in Bologna by CER and UNIBO.

BZN assessed the efficiency of the nutrient-saturated membranes as a fertiliser by laboratory-scale cultivation tests. The nutrients nitrogen, phosphorus and potassium in the soil were analysed, and plant leaf assessments have also been made by measuring these nutrients in the plant tissues.

2. Manufacturing and processing of the nanocellulose membrane material

Nanocellulose membrane materials were prepared and utilised for phosphate (PO_4^{3-}), nitrate (NO_3^-) and potassium (K^+) ions retention from water. For that, nanocellulose films were functionalised by two strategies, both involving a cationisation step to introduce positively charged quaternary ammonium groups on fibre surface: 1) bulk cationisation (water-based modification method involving etherification using glycidyl trimethylammonium chloride, GTAC) of pulp fibres prior to mechanical disintegration and 2) surface cationisation of already assembled nanocellulose membranes, e.g., interfacial modification of nanocellulose films by plasma-assisted gas-phase reaction (Figure 2). For strategy 1, softwood pulp fibres were first mercerised, followed by low-consistency cationisation (GTAC/AGU is 2.11), according to the pathway illustrated in Figure 3. Next, cationic pulp fibres were disintegrated into nanocellulose using the microfluidization technique. The obtained cationic nanofibers had a nitrogen content of 0.5%, as determined by elemental analysis, corresponding to the degree of substitution (DS) of 0.06.

Figure 2. Modular, R2R, pilot-scale commercial converting line (SutCo) for nanocellulose membrane preparation (left) and atmospheric plasma enhanced chemical vapour deposition unit for surface cationisation of already assembled nanocellulose membranes (right).

The second modification strategy relied on surface cationisation of already assembled nanocellulose membranes and was carried out by means of a Plasmaline® atmospheric plasma-enhanced chemical vapour deposition unit using glycidyl trimethylammonium chloride, GTAC, as precursor molecule to proceed with the thin-film deposition. During the experiments, the plasma power varied (250, 350, 450 and 550 W), whereas line speed and the number of passes were set to 0.5 m/min and 4, respectively.

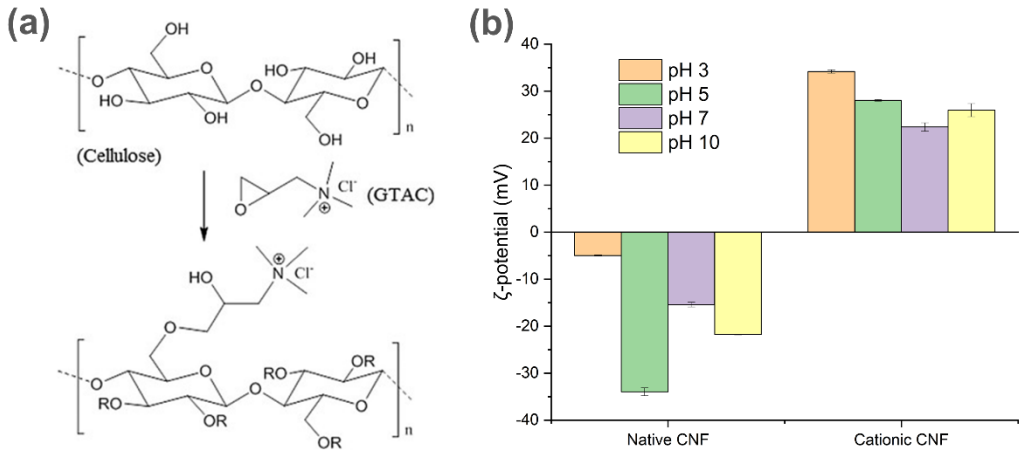


Figure 3.

Figure 3. Reaction pathway of GTAC substitution in cellulose (a) and ζ-potential measurements of prepared cationic nanocellulose indicating positive charge in a pH range 3-10.

XPS analysis was performed to examine the degree of substitution in the surface layers of the film through a determination of the amount of quaternary ammonium groups in the material. The relative elemental composition of all samples is shown in Table 1. Apart from carbon and oxygen, all samples also contained small amounts of nitrogen. Table 2 shows the relative ratios for the two components of nitrogen as compared to the total amount of nitrogen in the samples, as well as the relative amounts compared to the total signal from all elements in the surface layers of the samples.

Table 1. Relative concentrations of elements in the samples

Sample	C 1s%	O 1s%	N 1s%	Na 1s%	Cl 2p%
ref CNF-film	59.10	40.66	0.22	0.02	0.00
cat CNF	61.02	38.12	0.60	0.00	0.26
250	57.96	41.65	0.30	0.09	0.00
350	57.02	42.47	0.36	0.14	0.00
450	62.25	36.46	1.05	0.24	0.00
550	56.08	43.16	0.52	0.24	0.00

The smallest amount of nitrogen was detected in the reference CNF film, for which all nitrogen was in the form of amide- or NH-groups. The amount of quaternary nitrogen is greatest for the cationic CNF sample, with a slight increase in the amount seen over the first two plasma deposited samples but not for the last two. The total amount of nitrogen is, however, very much higher for the final two samples compared to the first two, perhaps suggesting that the trimethylammonium has dissociated during deposition.

Table 2. Relative amounts of the different components of nitrogen, as compared to the total amount of nitrogen in the samples. The final two column give the amount of amide/NH and quaternary nitrogen as compared to the signal from all elements in the samples.

Sample	amide/NH%	quaternary%	% of all elements	
			amide/NH	quaternary N
ref CNF-film	100,00	0,00	0,18	0,00
cat CNF	20.68	79.32	0.14	0.56
250	72.31	27.69	0.20	0.08
350	49.93	50.07	0.16	0.16
450	94.36	5.64	1.01	0.06
550	77.29	22.71	0.39	0.12

3. Initial lab tests with the membrane

To assess the nutrient uptake capacity of prepared membranes following the two selected strategies, several A5 size membranes (corresponding to ~1.5-3 g of cellulose) were immersed overnight under magnetic stirring in 5 litres beakers with 50 mg/l solutions of KNO_3 and NaH_2PO_4, as depicted in Figure 4. The nutrient concentrations before and after saturation were measured with a HACH Lange DR3900 spectrophotometer, and the results are summarised in Table 3. It is worth noting that nutrients sorption capacity was ~8 times higher for cationic nanocellulose-based membrane (bulk modification) compared to chemically unmodified membrane used as a reference. Surprisingly, the nutrients sorption capacity of the plasma-modified nanocellulose-based membrane (surface modification) was lower compared to the chemically unmodified membrane. The possible explanation might be that despite the successful introduction of positively charged quaternary ammonium groups on the nanocellulose membrane surface, highly cross-linked and water-impermeable layers (thickness few hundred nm) were deposited, which restricted nutrient penetration inside the bulk of the membrane and nutrient adsorption proceeded only on the surface. In contrast, nutrients were allowed to penetrate inside the structure of the unmodified membrane (thickness ~25 µm) due to diffusion phenomenon and were physically trapped within the nanoporous and highly entangled network structure of the nanocellulose membrane.

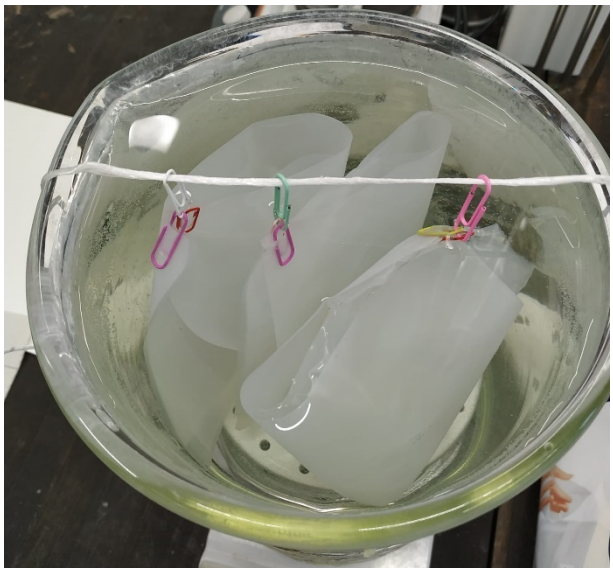


Figure 4. Nutrient uptake capacity measurements of prepared membranes

To further maximise the nutrient uptake capacity of nanocellulose membranes, cellulose cationisation was conducted in a heterogeneous method using Lödige 10 L high consistency (50% dry content) reactor, and GTAC/AGU was 1. Lowering water content in the reaction media resulted in increased reaction efficiency, and the obtained cationic nanofibers had a nitrogen content of ~1.4% as determined by elemental analysis, corresponding to the degree of substitution (DS) of 0.2, which is more than 3 times higher compared to the previous batch.

Planned work: New cationic nanocellulose membranes preparation and assessment of their nutrient uptake.

Table 3. Nutrient uptake capacity of prepared nanocellulose-based membranes (per dry membrane mass).

Sample	Nutrient absorption, mg/g (dry)		
	Unmodified membrane	Cationic (bulk)	Cationic (surface)
K^+	2.7	7.6	1.7
NO_3^-	1.1	8.2	0.6
PO_4^{3-}	2.0	11.3	0.5

4. Tests in a real environment

In order to test the membrane performance in a real environment and at dynamic conditions, a test at the Italian site was performed.

4.1 Description of the pilot site

The site in Italy is associated with Aquacampus, managed by CER, located in Budrio, near the city of Bologna (Italy). Among other solutions tested, a pilot plant (Figure 5) was constructed, integrating different WATERAGRI solutions such as farm wetlands, biochar and nitrocellulose membranes. The plant's purpose is to treat agricultural drainage water and to recover and reuse macronutrients for fertilisation, with the final scope of reducing the use of artificial compounds, thus closing the agricultural cycle.

Figure 5. The pilot plant at the Italian experimental site

4.2 Configurations of membrane

The membrane sheets were enclosed in a 60 cm long case that contained a framework built to keep the layers at a distance of 1 cm. The framework consisted of circular plastic bases, plastic rods and a net intended to provide rigidity to the material and prevent it from deforming under the water pressure and flow (Figure 6).

This arrangement was enveloped in the abovementioned 20 L case (Figure 7) equipped with an exhaust valve for pressure equilibration, self-compensating inlet drippers, allowing different flow applications, and an angle pipe outlet, where sampling was performed (Figure 8).

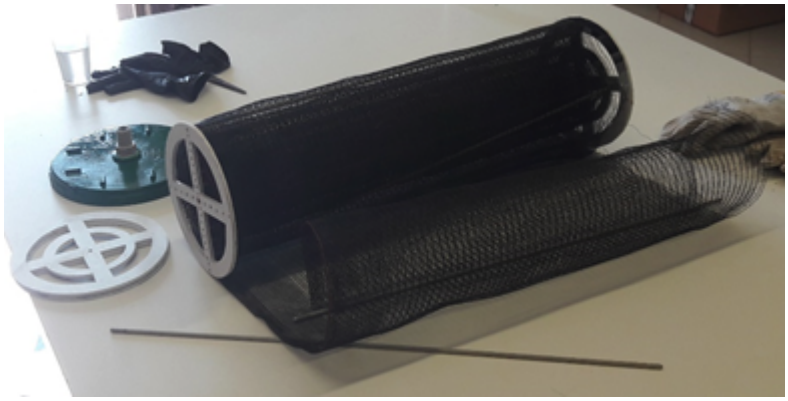


Figure 6. Net applied to the supporting frame

Figure 7. The membrane positioned in the case

Figure 8. Closed case during the test runs

4.3 Pilot tests

The membrane was tested at different flow rates and concentrations of applied nutrients to assess its performance in different experimental conditions. The flow rate ranged from 4 L h^{-1} to 16 L h^{-1}, with concentrations of NO_3^--N and PO_4^{3-}-P between 7 and 16 mg L^{-1} and 3.5 - 8 mg L^{-1}, respectively. Time zero corresponds to the moment at which the working solution first exited the outlet tap.

4.3.1 Test 1

The first test was performed by applying 7.5 and 3.5 mg L^{-1} of N-NO_3^--N and PO_4^{3-}-P, respectively, with 4 L h^{-1} of the working solution flow rate. Considering the low flow rate, the membrane casing was filled with a pre-mixed working solution containing the same concentrations as the influent solutions. This was done to reduce the outflow lag time from the first contact between the working solution and the membrane. The casing was then closed, and the test was carried out for 3 hours.

The recorded removal efficiencies (Figure 9) reached a relatively low peak of 9.3 and 16.0% between 40 and 60 min from the beginning of the test. On average, they resulted in 5.2 and 8.2%, dropping to 2.6 and 4.1% at the end of the test.

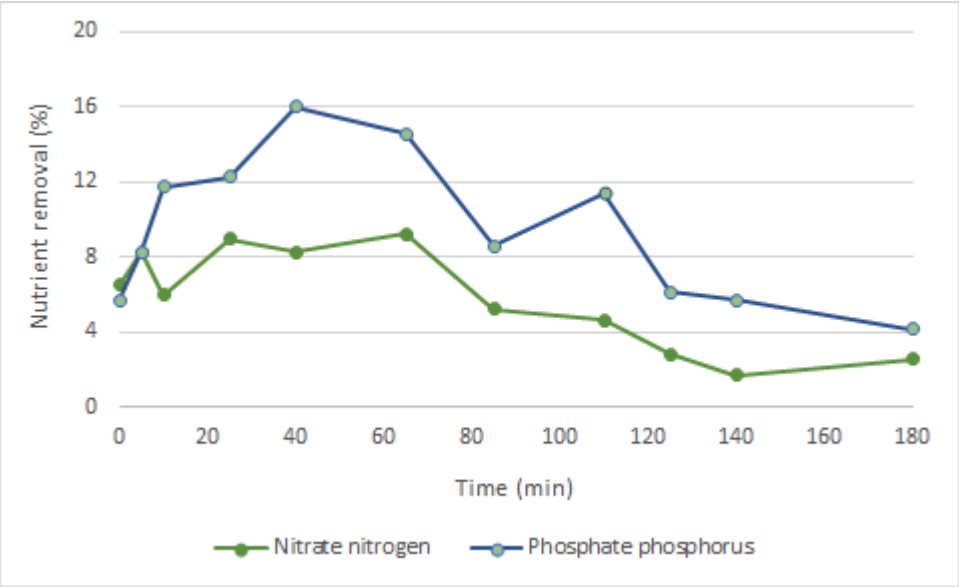


Figure 9. Removal of nutrients during the first test.

4.3.2 Test 2

During the second test, in order to overcome difficulties caused by a low flow rate, 15.6 and 7.5 mg L^{-1} of $N\text{-}NO_3^-$-N and PO_4^{3-}-P were respectively applied, with 16 L h^{-1} of the working solution flow rate. The working solution was directly injected into the casing, without pre-filling, like in the first test. Due to the higher flow rate and concentrations, the test lasted for 2 hours.

The removal efficiencies (Figure 10) peaked between the first 5 and 10 minutes, reaching 6.1 and 6.6% of abatement. On average, the removal capability remained low, i.e., 2.6 and 3.8%.

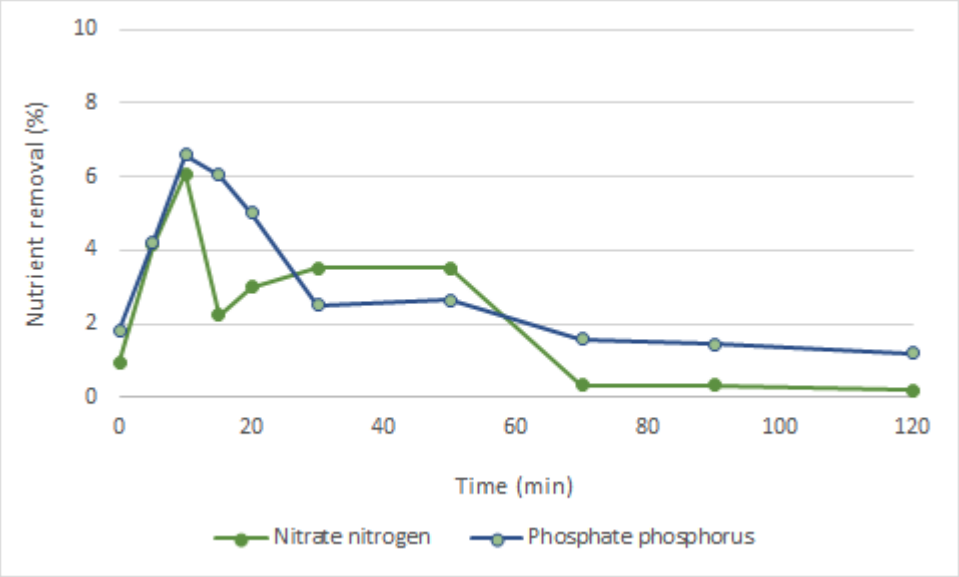


Figure 10. Removal of nutrients during the second test.

5. Laboratory scale cultivation tests for nutrient saturated membranes

The aim of the experiments performed by BZN was to assess the efficiency of the nutrient-saturated membranes as a possible fertiliser by laboratory-scale cultivation tests based on nitrogen, phosphorus and potassium content of the soil and plant tissues.

5.1 Materials and methods

Sandy soil with low nutrient content was filled into 7x7 cm pots till 2 cm from the top. 2x2 cm pieces were cut out from the control (unsaturated), phosphorus (NaH_2PO_4) saturated and nitrogen + potassium (KNO_3) saturated membranes that were prepared and provided by VTT. Each of these pieces was cut into thin slices (Figure 11. A). The slices were spread on the surface of the pots (Figure 11.B), then covered with an additional layer of soil (approx. 2 cm), and two holes were made with a conical centrifuge tube. Green coral lettuce 'Lollo Bionda' (*Lactuca sativa var. crispa*) seeds were sown into the holes (one seed in each hole, two seeds per pot) (Figure 11.C).

A. Cutting the membrane pieces

B. Membrane pieces spread on the soil surface

C. Lettuce seeds sown into the holes

Figure 11. Preparation of the plant experiments

Eight pots were set for each type of membrane (unsaturated, P-saturated, N+K-saturated, marked by MC, P, NK, respectively) and additional eight pots for control samples without membrane (marked by C). Pots were watered regularly and placed under artificial lights switched on from 8 AM to 6 PM. Germination of seeds was followed daily by recording the number of leaves. This cultivation test was repeated three times.

The nutrient content of the soil and plant leaves was determined at the end of the experiment. The extraction of soil and plant samples was made according to the methodology developed by Miles et al. (1983). The total nitrogen and phosphorus content of the extracts was measured by colorimetric determination of nitrate by

nitration of salicylic acid (Cataldo et al. 1975) and the vanadomolybdo-phosphoric acid colourimetric method (APHA, 2005), respectively. The potassium content of samples was measured by a HORIBA LAQUAtwin Compact Water Quality Meter.

5.2 Results

The experimental plots containing untreated membrane (MC), phosphorus-containing membrane (P), nitrogen and potassium-containing membrane (NK) and no membrane (C) were compared, based on seed germination, plant development and nutrient (N, P, K) measurements from soils and plant leaves.

Germination occurred simultaneously in all experimental settings. The number of germinated seeds in the plots containing different membranes followed the same kinetics and did not differ significantly during all three experiments.

The average number of leaves generally followed the same kinetics in the plots containing different membranes in all three experiments. There were some occasions when significant differences could be observed (e.g. on day 5 of the first experiment, the C group had a significantly lower average leaf number than the P and NK groups, and on day 29 of the third experiment, the C group had significantly lower average leaf number than the NK group), but this difference existed for one day only, and did not follow any trend. Figure 12 shows the results of the first experiment for both germination and the number of leaves.

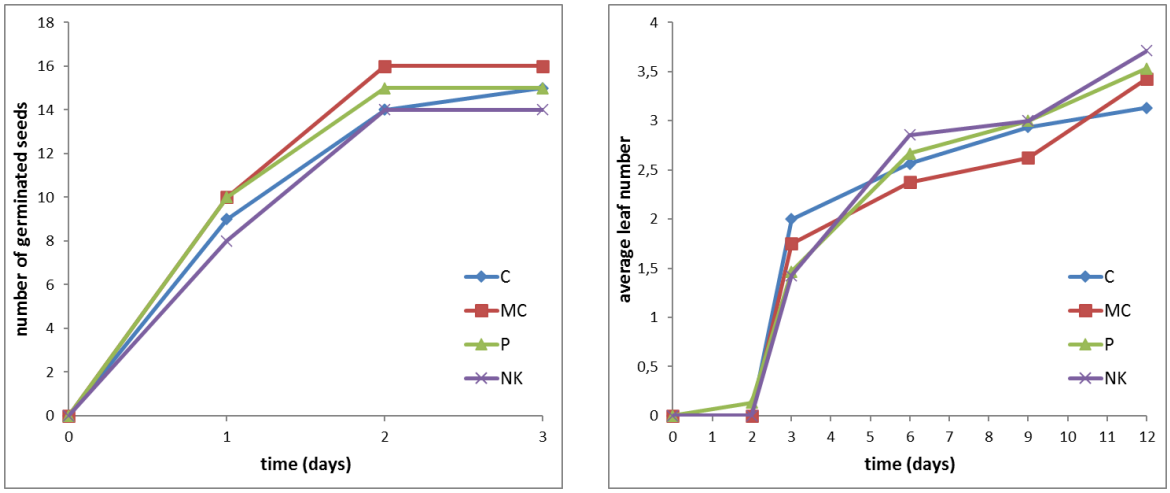
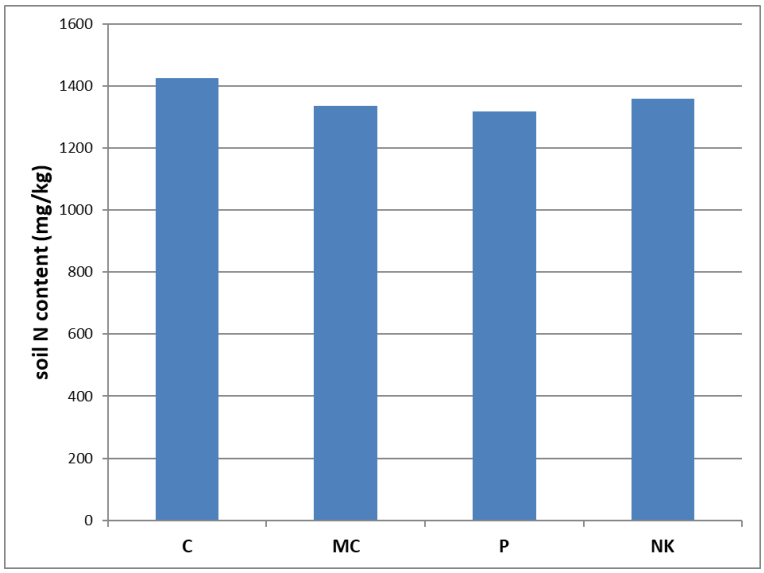
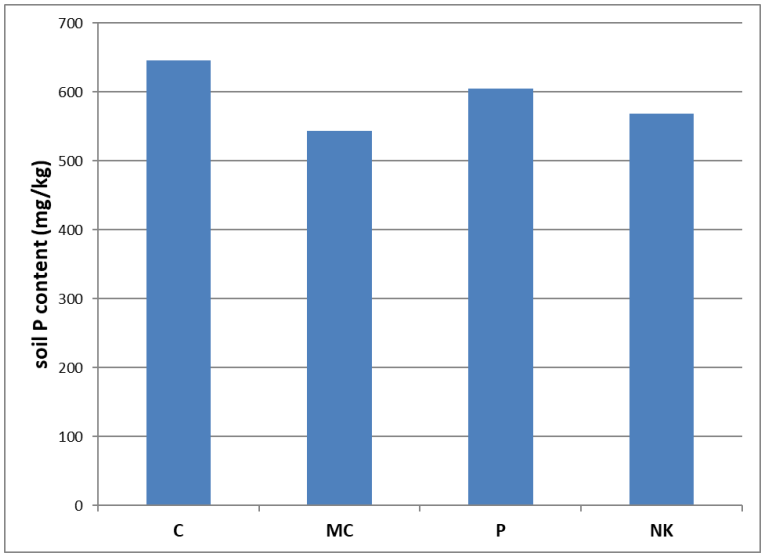


Figure 12. Number of germinated seeds and average leaf number in the first experiment (C: no membrane, MC: unsaturated membrane, P: P-saturated membrane, NK: N+K-saturated membrane)

The nutrient content of the soil amended with membranes was not higher compared with the control group containing no membrane (Figure 13.). The nutrient content was similar in all groups in most cases. There was no significant difference in the nutrient content of the plant leaves either among the different groups (Figure 14.).

Based on the experiments described above, nutrient saturated membranes were not capable of significantly increasing the nutrient content of the soil or the plants. The addition of membranes did not affect the germination and development of plants. It should be noted that the amount of nutrients adsorbed to the cationic nanocellulose membrane was low (111 mg/m^2, 219 mg/m^2, and 459 mg/m^2 for N, P, K, respectively, according to the results of VTT), and these amounts cannot be expected to have a significant effect on the parameters investigated. The membrane is still under development at VTT, and partners are planning further cultivation tests with the newly developed version having a higher adsorption capacity.





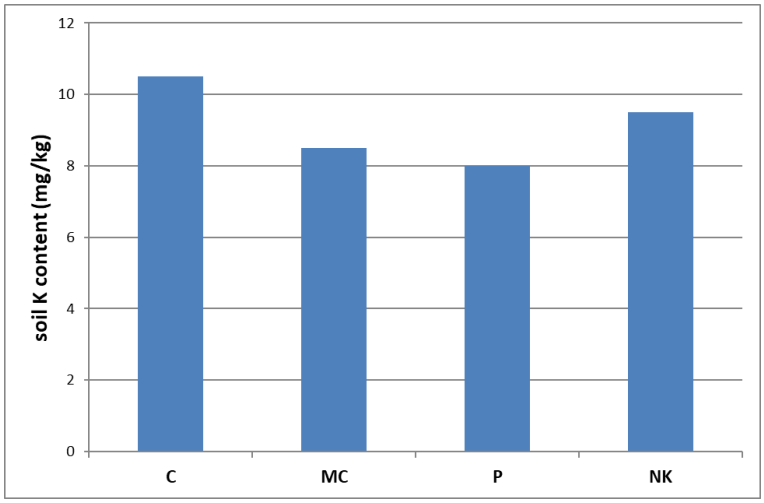


Figure 13. Nutrient content of soil in the second experiment (C: no membrane, MC: unsaturated membrane, P: P-saturated membrane, NK: N+K-saturated membrane)

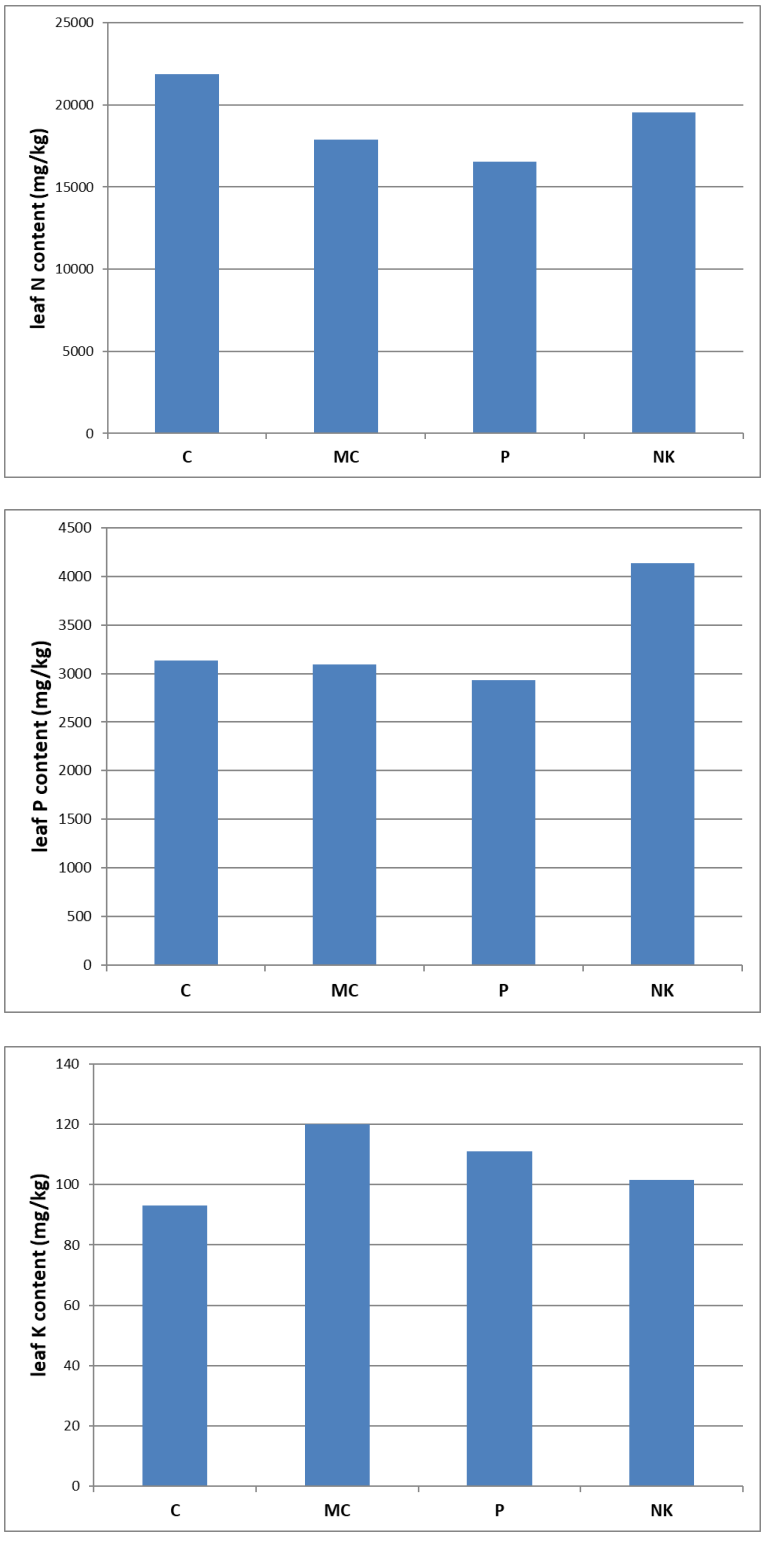


Figure 14. Nutrient content of leaves in the second experiment (C: no membrane, MC: unsaturated membrane, P: P-saturated membrane, NK: N+K-saturated membrane)

6. Conclusion and outlook

Nutrient recovery from agricultural runoff with biobased membranes is a new approach enabling the return of the leached nutrients back to the cultivation and their original purpose, which is fertilising. However, the concept is very new and needs further fine-tuning to reach practical implementation. The work is continuing with new configurations allowing more efficient uptake of macronutrients.

The fertilising effect of saturated membranes was found to be minute. However, acknowledging that the amount of nutrients adsorbed to the membranes are not sufficient to act as fertilisers per se, returning the recovered nutrients back to the soil is a true circular solution and also provides a means to perform the treatment of runoffs with zero residual waste. It is also very important to test the membrane in different operating conditions (e.g., hydraulic retention time, constant or intermittent flow rate, influent nutrient concentrations) since it still needs to be optimised in order to maximise its impact. To this view, the tests done at the Italian field site are a step in the right direction, enabling membrane testing in the real environment, but they should be repeated in the future involving a new and improved type of membrane.

It is to be noted that at the time of this deliverable submission, the work is going on, and the latest results of new, potentially more efficient configurations and structures were not yet in hands. This deliverable will be updated with the latest information at the end of the project.

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